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(54) **Fiber-reinforced composites having having continuously varied fibre density across the month of the base layer, and manufacturing method thereof.**

(57) Disclosed is fiber-reinforced composites having a gradient function having an excellent mechanical strength characteristic, good oxidation-resistance and good fracture toughness even at high temperatures not lower than 1500 °C. The fiber-reinforced composite according to the present invention includes: a base formed of carbon-fiber reinforced composites having a good mechanical strength characteristic and good fracture toughness; and a surface portion covering the base and formed of ceramic-fiber reinforced composites having good oxidation-resistance, wherein the carbon content rate of the base decreases almost successively from a central portion of the base to an interface portion of the base and the surface portion. This results in the fiber-reinforced composite which has good oxidation-resistance, a good mechanical strength characteristic and good fracture toughness even at high temperatures not lower than 1500 °C and in which an abrupt change in respective thermal expansion coefficients of the base and the surface portion in the interface therebetween is reduced by its gradient composition.

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BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to fiber-reinforced composites and a method of manufacturing such composites and, more particularly, to fiber-reinforced composites having an excellent mechanical strength characteristic, good oxidation-resistance, good erosion-resistance and good fracture toughness at high temperatures, and a method of manufacturing such composites.

Description of the Background Art

Conventionally, as composites for use in the field of aeronautics and space, such fiber-reinforced composites are expected that carbon or ceramics such as silicon carbide is formed as a matrix which is reinforced with carbon fiber or ceramic fiber such as of silicon carbide. Of such fiber-reinforced composites, a carbon-fiber reinforced composite having carbon fiber as a reinforcing material exhibits a superior specific mechanical strength (strength per unit weight) and higher fracture toughness even at high temperatures above 1500 ° C.

Since the carbon-fiber reinforced composite includes carbon fiber, however, the composite has a disadvantage that it has poor oxidation-resistance and poor erosion-resistance at high temperatures.

Thus, in order to eliminate such a disadvantage, a coated layer made of silicon carbide or silicon nitride having excellent oxidation-resistance is formed on a surface. However, since a thermal expansion coefficient of the carbon-fiber reinforced composite is extremely low as compared to that of the coated layer, there is a problem that thermal-cracks are produced in the coated layer in a heat cycle. Consequently, it has been conventionally difficult to provide fiber-reinforced composites having good oxidation-resistance and good erosion-resistance.

Further, as reinforcing materials, there are ceramic-fiber reinforced composites in which the matrix of silicon carbide or silicon nitride is reinforced with ceramic fiber such as silicon carbide fiber. Since both the reinforcing fiber and the matrix of the ceramic-fiber reinforced composites are formed of substances having good oxidation-resistance and good erosion-resistance, the composites are excellent in oxidation-resistance and good erosion-resistance at high temperatures and require no oxidation-resistive coated layer. Taking silicon carbide fiber as an example, however, since there occurs such a phenomenon that the mechanical strength of silicon carbide fiber decreases at approximately 1200 ° C or more, this composite has a poor mechanical strength characteristic at high temperatures.

SUMMARY OF THE INVENTION

One object of the present invention is to obtain fiber-reinforced composites having an excellent mechanical strength characteristic, high oxidation-resistance, high erosion-resistance and good fracture toughness even at high temperatures not lower than 1500 ° C.

Another object of the present invention is to form fiber-reinforced composites having a gradient function.

A further object of the present invention is to facilitate manufacture of fiber-reinforced composites having a gradient function in a method of manufacturing fiber-reinforced composites.

According to one aspect of the present invention, a fiber-reinforced composite includes: an inner base formed of a carbon-fiber reinforced composite in which a first matrix including heat resisting ceramics is reinforced with carbon fiber; and two surface portions formed on both surfaces of the inner base and formed of a ceramic-fiber reinforced composite in which a second matrix including heat resisting ceramics is reinforced with ceramic fiber, and the rate of carbon fiber content in the inner base decreases almost successively from a central portion of the inner base to an interface portion between the inner base and the surface portions.

In operation, since the ceramic-fiber reinforced composite having good oxidation-resistance and good erosion-resistance is employed for the two surface portions, and the carbon-fiber reinforced composite having a good mechanical strength characteristic and good fracture toughness is employed for the inner base, this fiber-reinforced composite of the present invention has an excellent mechanical strength characteristic under high temperatures and excellent fracture toughness as well as excellent oxidation-resistance and excellent erosion-resistance under high temperatures. In addition, since the carbon-fiber content rate of the inner base decreases almost successively from the central portion of the inner base to the interface between the inner base and the surface portions, a thermal expansion coefficient successively increases from the central portion of the inner base toward the interface between the inner base and the

surface portions. Accordingly, the difference between the thermal expansion coefficient of the surface portions and that of the inner base is further decreased in the interface between the surface portions and the inner base as compared to the conventional. This enables prevention of thermal-cracks or fracture in a heat cycle.

According to another aspect of the present invention, a fiber-reinforced composite includes: a base formed of a carbon-fiber reinforced composite in which a first matrix including ceramics is reinforced with carbon fiber; and a surface portion formed on one surface of the base and formed of a ceramic-fiber reinforced composite in which a second matrix including ceramics is reinforced with ceramic fiber, and the rate of carbon fiber content in the base decreases almost successively from a central portion of the base to an interface between the base and the surface portion.

In operation, since the ceramic-fiber reinforced composite having good oxidation-resistance and good erosion-resistance is employed for one surface portion of the base requiring oxidation-resistance, and the carbon-fiber reinforced composite having a good mechanical strength characteristic and good fracture toughness is employed for the base being the other portions, this fiber-reinforced composite has an excellent mechanical strength characteristic under high temperatures and excellent fracture toughness as well as excellent oxidation-resistance and excellent erosion-resistance under high temperatures. In addition, since the carbon fiber content rate decreases almost successively from the central portion of the base toward the interface between the base and the surface portion, a thermal expansion coefficient is successively increased from the central portion of the base toward the interface between the base and the surface portion. Accordingly, the difference between the thermal expansion coefficient of the surface portion and that of the base in the interface between the base and the surface portion is further decreased as compared to the conventional. This results in prevention of thermal-cracks or fracture in a heat cycle.

According to one aspect of the present invention, a method of manufacturing a fiber-reinforced composite includes the steps of: forming a plurality of sheets for a base, formed of a carbon-fiber reinforced composite in which a first matrix including ceramics is reinforced with carbon fiber and having different rates of carbon fiber content; forming a plurality of sheets for a surface portion, formed of a ceramic-fiber reinforced composite in which a second matrix including ceramics is reinforced with ceramic fiber; forming a laminated body by laminating the plurality of base sheets so that the carbon fiber content rate of the base sheets decreases centrifugally from its center to the outside and by laminating the sheets for the surface portion on the base sheets of two outermost layers; and subjecting the laminated body to heat treatment and then to pressure sintering.

In operation, the plurality of base sheets having different carbon fiber content rates and the plurality of surface portion sheets made of ceramic-fiber reinforced composites are formed separately. After that, the base sheets are laminated to obtain a predetermined gradient composition, and the surface portion sheets are laminated thereon. The resultant laminated body is then subjected to heat treatment and pressure sintering. Accordingly, a fiber-reinforced composite having a gradient composition can easily be fabricated.

According to another aspect of the present invention, a method of manufacturing a fiber-reinforced composite includes the steps of: forming a plurality of sheets for a base, made of a carbon-fiber reinforced composite in which a first matrix including ceramics is reinforced with carbon fiber and having different carbon fiber content rates; forming a sheet for a surface portion, made of a ceramic-fiber reinforced composite in which a second matrix including ceramics is reinforced with ceramic fiber; forming a laminated body by laminating the plurality of base sheets so that the carbon fiber content rate of the base sheets decreases centrifugally from its center to one outside and by laminating the surface portion sheet on the base sheet of an outermost layer having a decreased carbon fiber content rate; and subjecting the laminated body to heat treatment and then pressure sintering.

In operation, the plurality of base sheets having different carbon fiber content rates and the surface portion sheet made of the ceramic-fiber reinforced composite are formed separately. Then, the plurality of base sheets having different carbon fiber content rates are laminated to obtain a predetermined gradient composition, and the surface portion sheet is laminated on the base sheet of one outermost layer having a lower carbon fiber content rate. The resultant laminated body is subjected to heat treatment and then pressure sintering. Accordingly, a fiber-reinforced composite having a gradient composition can easily be fabricated.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

A description will first be made on the essence of the present invention prior to a description of examples. In the present invention, one or both of surface portions requiring oxidation-resistance and erosion-resistance are formed of ceramic-fiber reinforced composites having excellent oxidation-resistance,

and the other portions are formed of carbon (C)-fiber reinforced composites having an excellent mechanical strength characteristic and excellent fracture toughness. Accordingly, the fiber-reinforced composite of the present invention has a good mechanical strength characteristic under high temperatures and good fracture toughness as well as good oxidation-resistance and good erosion-resistance under high temperatures.

Particularly, in order to obtain sufficient oxidation-resistance, it is desirable that the ceramic-fiber reinforced composites constituting the surface portions have fine texture with no pores. For this purpose, an oxidation-resisting minute coated layer made of silicon carbide (SiC) or silicon nitride (Si_3N_4) is preferably provided on one or both of the surfaces made of the ceramic-fiber reinforced composites. Such a coated layer can be formed by employing a conventional thin film forming technique such as a CVD method. In addition, since the fiber-reinforced composite of the present invention has a gradient composition, an abrupt change in thermal expansion coefficient of an interface between carbon-fiber reinforced composite constituting a base and ceramic-fiber reinforced composites constituting surface portions can be decreased as compared to the conventional composite. A detailed structure of the fiber-reinforced composite of the present invention is shown in Tables 1 and 2 below.

Table 1

SiC/Si_3N_4	$V_f = 55$	$V_m = 45$	$V_p = 0$	$\alpha = 3.0$	- Surface	
C/Si_3N_4	$V_f = 40$	$V_m = 55$	$V_p = 5$	$\alpha = 2.4$		
C/Si_3N_4	$V_f = 50$	$V_m = 45$	$V_p = 5$	$\alpha = 1.6$		
C/Si_3N_4	$V_f = 60$	$V_m = 35$	$V_p = 5$	$\alpha = 1.0$		
C/Si_3N_4	$V_f = 80$	$V_m = 15$	$V_p = 5$	$\alpha = 0.5$	Inner base	
C/Si_3N_4	$V_f = 60$	$V_m = 35$	$V_p = 5$	$\alpha = 1.0$	(Gradient Composition)	
C/Si_3N_4	$V_f = 50$	$V_m = 45$	$V_p = 5$	$\alpha = 1.6$		
C/Si_3N_4	$V_f = 40$	$V_m = 55$	$V_p = 5$	$\alpha = 2.4$		
SiC/Si_3N_4	$V_f = 50$	$V_m = 45$	$V_p = 0$	$\alpha = 3.0$	- Surface	

V_f : Rate of fiber volume content (%)
V_m : Rate of matrix volume content (%)
α : Thermal expansion coefficient (x $10^{-6}K^{-1}$)

Table 2

SiC/SiC	$V_f = 55$	$V_m = 45$	$V_p = 0$	$\alpha = 3.5$	- Surface	
C/SiC	$V_f = 40$	$V_m = 55$	$V_p = 5$	$\alpha = 2.6$		
C/SiC	$V_f = 50$	$V_m = 45$	$V_p = 5$	$\alpha = 1.9$	Base	
C/SiC	$V_f = 60$	$V_m = 35$	$V_p = 5$	$\alpha = 1.3$	(Gradient Composition)	
C/SiC	$V_f = 80$	$V_m = 15$	$V_p = 5$	$\alpha = 0.6$		

V_f : Rate of fiber volume content (%)
V_m : Rate of matrix volume content (%)
V_p : Porosity (%)
α : Thermal expansion coefficient (x $10^{-6}K^{-1}$)

With reference to Tables 1 and 2 above, the carbon fiber volume content rate of an inner base shown in Table 1 and a base shown in Table 2, made of carbon-fiber reinforced composites (C/Si_3N_4 or C/SiC) is almost successively decreased toward surfaces shown in Tables 1 and 2, formed of SiC fiber composites (SiC/Si_3N_4 or SiC/SiC). At the same time, the matrix volume content rate is almost successively increased. Accordingly, since a thermal expansion coefficient of the overall structure including the surfaces varies almost successively, an abrupt change in thermal expansion coefficient between the (inner) base and the surfaces is reduced, thereby decreasing thermal stresses. This enables an effective reduction in occurrence of thermal-cracks, separation, fracture and the like in the surfaces.

The fiber-reinforced composite having the above composition was fabricated in practice in the following Examples 1-3.

Example 1

SiC powder of 2μm in average grain size was employed as a matrix. This SiC powder was mixed with a slight amount of Al_2O_3 powder and then kneaded with acrylamide resin. The mixture was then applied onto a fabric cloth of SiC fiber. As a result, a SiC/SiC composite sheet made of SiC fiber and SiC powder was obtained. A mass ratio of the fiber/applied matter of the SiC/SiC composite sheet was set to 0.95.

Then, SiC powder of 2μm in average grain size was employed as a matrix, and this SiC powder was mixed with a slight amount of Al_2O_3 powder and then kneaded with acrylamide resin. The mixture was applied in different amounts onto the fabric of carbon fiber. As a result, C/SiC composite sheets a to c formed of carbon fiber and SiC powder were obtained. Mass ratios of the fiber/applied matter of these C/SiC composite sheets were as follows: composite sheet a, 0.88; composite sheet b, 0.91; and composite sheet c, 0.95.

Combining the composite sheets a to c resulted in the following laminated body. That is, 21 composite sheets in total were laminated in the following order: SiC/SiC composite sheets (3 sheets), C/SiC composite sheets a (3), C/SiC composite sheets b (3), C/SiC composite sheets c (3), C/SiC composite sheets b (3), C/SiC composite sheets a (3), and SiC/SiC composite sheets (3). After that, this laminated body was heated at 500°C for three hours and volatile matter was removed. The resultant body was then subjected to pressure sintering at 2000°C under a pressure of 200Kg/cm^2 for two hours. Accordingly, a composite (hereinafter referred to as C-SiC/SiC) of 50mm in length by 50mm in width by 4mm in thickness was manufactured. This composite has a gradient function and is formed of silicon carbide (SiC) reinforced with carbon (C) fiber and silicon carbide (SiC) fiber. For the C-SiC/SiC sample thus fabricated, its bending strength at room temperature and at 1500°C and a fracture toughness value K_{IC} by an SEPB method was measured. Moreover, a laminated surface of the sample was covered with a mask and held in the atmosphere at 1700°C for one hour. From changes in the mass of the sample before and after it was held in the atmosphere, a mass loss of the sample after oxidation was obtained.

As reference examples (four examples), manufactured composites were a SiC/SiC composite of a uniform composition in which a SiC matrix is reinforced only with SiC fiber (a mass ratio of SiC fiber/SiC matrix: 0.95), and C/SiC composites A to C of a uniform composition in which a SiC matrix is reinforced only with carbon (C) fiber (mass ratios of C fiber/SiC matrix: A, 0.88; B, 0.91; and C, 0.95). The same test as above was also carried out with respect to those four reference examples.

The result of the test with respect to Example 1 and the above four reference examples is shown in Table 3 below.

Table 3

Composites	Thermal Expansion Coefficients ($\times 10^{-6}$)	Bending Strength (MPa)		K_{IC} ($MPam^{1/2}$)		Mass Loss ($/mg \cdot cm^{-2}$)
		Room Temp.	1500°C	Room Temp.	1500°C	
C-SiC/SiC	——	320	330	30	30	2.1
SiC/SiC*	3.5	220	85	15	15	2.2
C/SiC A*	2.4	140	135	16	16	23.2
C/SiC B*	1.5	210	220	22	22	46.8
C/SiC C*	0.7	350	360	35	34	80.2

Note: Marks * denote reference examples.

Referring to Table 3 above, it is noted that with respect to C-SiC/SiC in Example 1, the mass loss is considerably small as compared to those of reference examples A-C. It is also noted that the bending strength of C-SiC/SiC in Example 1 is considerably large as compared to that of SiC/SiC in the reference example. It is further noted that the fracture toughness value K_{IC} of C-SiC/SiC in Example 1 is larger than those of the reference examples (SiC/SiC, C/SiC (A) and C/SiC (B)).

As mentioned above, it is understood that the C-SiC/SiC composite of Example 1 has an excellent mechanical strength characteristic, excellent oxidation-resistance and high fracture toughness even at high temperatures not lower than 1500 ° C.

Example 2

Si_3N_4 powder of 2m in average grain size was employed as a matrix. This Si_3N_4 powder was mixed with a slight amount of Al_2O_3 powder and then kneaded with acrylamide resin. This mixture was applied onto the fabric of SiC fiber. As a result, a SiC/Si_3N_4 composite sheet made of SiC fiber and Si_3N_4 powder was obtained. A mass ratio of the fiber/applied matter of the SiC/Si_3N_4 composite sheet was set to 0.94.

Then, Si_3N_4 powder of 2μm in average grain size was employed as a matrix. This Si_3N_4 powder was mixed with a slight amount of Al_2O_3 powder and then kneaded with acrylamide resin. This mixture was applied in different amounts to the fabric of carbon fiber. As a result, C/Si_3N_4 composite sheets d to f made of carbon fiber and Si_3N_4 powder were obtained. Mass ratios of the fiber/applied matter of those C/Si_3N_4 composite sheets were: composite sheet d, 0.87; e, 0.91; and f, 0.94.

Combining those composite sheets resulted in the following laminated body. That is, 20 composite sheets in total were laminated in the following order: SiC/Si_3N_4 composite sheets (5 sheets), C/Si_3N_4 composite sheets d (5), C/Si_3N_4 composite sheets e (5), and C/Si_3N_4 composite sheets f (5). After that, the laminated body was heated at 500 ° C for three hours and its volatile matter was removed. The resultant laminated body was then pressure-sintered at 2000 ° C under a pressure of 200Kg/cm^2. This resulted in the manufacture of a composite (hereinafter referred to as C-SiC/Si_3N_4) of 50mm in length by 50mm in width by 4.2mm in thickness, having a gradient function and formed of silicon nitride (Si_3N_4) reinforced with carbon (C) fiber and silicon carbide (SiC) fiber.

For the C-SiC/Si_3N_4 sample thus manufactured, its bending strength at room temperature and 1500 ° C (bending strength in a direction in which tensile load was applied to the C/Si_3N_4 composite), and its fracture toughness value K_{IC} by the SEPB method were measured. Also, a laminated surface and a C/Si_3N_4 composite surface of the corresponding sample were covered with a mask and then held in the atmosphere at 1500 ° C for an hour. From changes in the mass of the sample before and after it was held in the atmosphere, a mass loss of the sample after oxidation was obtained.

As reference examples (four examples), manufactured composites were a SiC/Si_3N_4 composite of a uniform composition in which a Si_3N_4 matrix is reinforced only with SiC fiber (a mass ratio of SiC fiber/Si_3N_4 matrix is 0.94), and C/Si_3N_4 composites D to F of a uniform composition in which an Si_3N_4 matrix is reinforced only with carbon (C) fiber (mass ratios of carbon (C) fiber/Si_3N_4 matrix are: composite D, 0.87; E, 0.91; and F, 0.94). The same test as above was also carried out with respect to those four reference examples.

With respect to the composite of Example 2 and those of the four reference examples thus manufactured, the result of the test is shown in Table 4 below.

Table 4

Composites	Thermal Expansion Coefficients ($\times 10^{-6}$)	Bending Strength (MPa)		K_{IC} (MPam$^{1/2}$)		Mass Loss (/mg·cm^{-2})
		Room Temp.	1500°C	Room Temp.	1500°C	
C-SiC/Si_3N_4	——	440	330	36	36	2.4
SiC/Si_3N_4*	3.0	320	103	13	13	3.5
C/Si_3N_4 D*	2.2	190	185	16	17	23.2
C/Si_3N_4 E*	1.2	278	284	21	22	49.9
C/Si_3N_4 F*	0.5	475	465	38	38	74.3

Note: Marks * denote reference examples.

Referring to Table 4 above, it is noted that the mass loss of C-SiC/Si_3N_4 of Example 2 is considerably smaller than those of C/Si_3N_4 composites D to F of the reference examples. This demonstrates that C-SiC/Si_3N_4 of this example has good oxidation-resistance. It is also noted that the bending strength of C-SiC/Si_3N_4 of Example 2 is superior particularly at high temperatures to that of SiC/Si_3N_4 of the reference example. It is further noted that the fracture toughness value K_{IC} of C-SiC/Si_3N_4 of Example 2 is higher than

those of SiC/Si_3N_4 and C/Si_3N_4 D to F of the reference examples.

As described above, it is understood that the composite of Example 2 has good oxidation-resistance, good mechanical strength characteristic and good fracture toughness at high temperatures not lower than 1500 °C.

Example 3

SiC powder of 2μm in average grain size was employed as a matrix. This SiC powder was mixed with a slight amount of Al_2O_3 powder and then kneaded with acrylamide resin. This mixture was then applied onto the cloth of Si-C-N fiber, so that a Si-C-N/SiC composite sheet formed of Si-C-N fiber and SiC powder was obtained. A mass ratio of the fiber/applied matter of the Si-C-N/SiC composite sheet was 0.94.

Then, B_4C powder of 2μm in average grain size was employed as a matrix. This B_4C powder was mixed with a slight amount of Al_2O_3 powder and then kneaded-with acrylamide resin. This mixture was then applied in different amounts onto the cloth of carbon fiber, so that C/B_4C composite sheets g to i formed of carbon fiber and B_4C powder were obtained. Mass ratios of the fiber/applied matter of those C/B_4C composite sheets were as follows: composite sheet g, 0.87; h, 0.91; and i, 0.94.

Combining those composite sheets resulted in the following laminated body. That is, 20 composite sheets in total were laminated in the following order: Si-C-N/SiC composite sheets (5 sheets), C/B_4C composite sheets g (5), C/B_4C composite sheets h (5), and C/B_4C composite sheets i (5). After that, the laminated body was heated at 500 °C for three hours and its volatile matter was removed. The resultant laminated body was then pressure-sintered at 1800 °C under a pressure of 200Kg/cm^2 for two hours. Accordingly, a composite (hereinafter referred to as C-, Si-C-N/B_4C-SiC) of 50mm in length by 50mm in width by 3.9mm in thickness was manufactured. This composite has a gradient function including B_4C and SiC reinforced with carbon (C) fiber and Si-C-N fiber.

With respect to the C-,Si-C-N/B_4C-SiC sample thus manufactured, its bending strength at room temperature and at 1500 °C (a bending strength in a direction in which tensile strength is applied to the C/B_4C composite side) and a fracture toughness value K_{IC} by SEPB method were measured. Also, a laminated surface and a B_4C composite surface of the corresponding sample were covered with a mask and then held in the atmosphere at 1700 °C for an hour. From changes in the mass of the sample before and after it was held in the atmosphere, a mass loss of the sample after oxidation was obtained.

In addition, with the above-described C-,Si-C-N/B_4C-SiC sample used as a base material, an elaborate SiC coated layer was formed to a thickness of approximately 100μm on the surface of the Si-C-N/SiC composite surface on conditions of 1500 °C and 100 Torr by a CVD method using $SiCl_4$, CH_4 and H_2 as material gas. For this SiC coated sample also, like the foregoing sample, its bending strength at room temperature and at 1500 °C and its fracture toughness value by the SEPB method were obtained. Also, from changes in the mass of the sample before and after it was held in the atmosphere at 1700 °C for an hour, a mass loss of the sample after oxidation was obtained.

As reference examples, there were manufactured a Si-C-N/SiC composite of a uniform composition in which a SiC matrix is reinforced only with Si-C-N fiber (a mass ratio of Si-C-N fiber/SiC matrix is 0.94), and C/B_4C composites G to I of a uniform composition in which a B_4C matrix is reinforced only with carbon (C) fiber (mass ratios of C fiber/B_4C matrix are: G, 0.86; H, 0.91; and I, 0.93). The same test as above was carried out also for those four reference examples.

The result of the test for the composite of Example 3 and those of the four reference examples thus manufactured is shown in Table 5 below.

Table 5

Composites	Thermal Expansion Coefficients ($\times 10^{-6}$)	Bending Strength (MPa)		K_{IC} ($MPam^{1/2}$)		Mass Loss ($/mg \cdot cm^{-2}$)
		Room Temp.	1500°C	Room Temp.	1500°C	
C-,Si-C-N/B_4C-SiC	—	315	305	33	32	0.2
SiC coat sample	—	315	306	33	32	0.0
Si-C-N/SiC*	3.0	215	100	13	13	0.2
C/B_4C G*	2.3	155	145	15	16	30.2
C/B_4C H *	1.4	215	222	21	22	85.2
C/B_4C I*	0.4	330	298	34	34	125.3

Note: Marks * denote reference examples.

Referring to the above Table 5, it is noted that the mass loss of C-,Si-C-N//B_4C-SiC of Example 3 is considerably lower than those of C/B_4C (G to I) of the reference examples. This indicates that C-,Si-C-N/B_4C-SiC of Example 3 has good oxidation-resistance. It is also noted that the bending strength of C-,Si-C-N/B_4C-SiC of Example 3 is superior particularly at a high temperature of 1500° C to that of Si-C-N/SiC of the reference example. It is further noted that the fracture toughness value K_{IC} of C-,Si-C-N/B_4C-SiC of

Example 3 is higher than those of Si-C-N/SiC, C/B_4C (G to I) of the reference examples. As shown above, C-,Si-C-N/B_4C-SiC of Example 3 has excellent oxidation-resistance, an excellent mechanical strength characteristic and excellent fracture toughness at high temperatures not lower than 1500°C. It is further noted that C-,Si-C-N/B_4C-SiC of Example 3 having its Si-C-N/SiC composite surface covered with a SiC coated layer is superior in oxidation-resistance to that of Example 3.

As described above, in one fiber-reinforced composite of the present invention, an inner base is formed of carbon-fiber reinforced composites having an excellent mechanical strength characteristic and excellent fracture toughness, two surface portions formed on the both surfaces of the inner base are formed of ceramic-fiber reinforced composites having excellent oxidation-resistance, and the carbon fiber content rate of the inner base is made to decrease almost successively from the central portion of the inner base toward the interface between the inner base and the surface portions. Because of this structure, it is possible to provide the fiber-reinforced composite exhibiting a good mechanical strength characteristic, good oxidation-resistance and good fracture toughness even at high temperatures not lower than 1500°C. Further, forming the inner base having a gradient composition makes it possible to successively change thermal expansion coefficient α between the base and the surface portions at the interface therebetween. This makes it possible to prevent a fracture of the composite and occurrence of thermal-cracks in the coated layer in a heat cycle and also prevent a deterioration in oxidation-resistance.

In another fiber-reinforced composite of the present invention, a base is formed of carbon-fiber reinforced composites having a good mechanical strength characteristic and good fracture toughness, a surface portion covering one surface of the base is formed of ceramic-fiber reinforced composites having good oxidation-resistance, and the carbon-fiber content rate of the base is made to decrease almost successively from the central portion of the base toward the interface between the base and the surface portion. Because of this structure, the surface portion exposed under high temperatures can obtain excellent oxidation-resistance and an excellent mechanical strength characteristic and excellent fracture toughness as the composite even at high temperatures not lower than 1500°C. Further, forming the base having a gradient composition makes it possible to successively change thermal expansion coefficient α between the base and the surface portion at the interface therebetween. This results in effective prevention of a fracture of the composite and thermal-cracks in the surface portion in a heat cycle and a deterioration in oxidation-resistance.

In one method of manufacturing a fiber-reinforced composite according to the present invention, a plurality of base sheets formed of carbon-fiber reinforced composites and having different rates of carbon-fiber content and a sheet for a surface portion, formed of ceramic-fiber reinforced composites are formed separately. The base sheets are laminated so that their carbon fiber content rates decrease from the center to the outside, and also the surface portion sheet is laminated on outermost layers of both sides of the base. A resultant laminated body is then subjected to heat treatment and then pressure-sintering, whereby a fiber-reinforced composite having excellent oxidation-resistance, a good mechanical strength characteristic and excellent fracture toughness can easily be manufactured at high temperatures not lower than 1500°C.

In another method of manufacturing a fiber-reinforced composite according to the present invention, a plurality of sheets for a base, formed of carbon-fiber reinforced composites and having different rates of carbon fiber content and a sheet for a surface portion, made of ceramic-fiber reinforced composites are separately formed. The base sheets are laminated so that their carbon fiber content rates decrease from the center toward one outside, and the surface portion sheet is laminated on the base sheet of an outermost layer, the carbon-fiber content rate of which is decreased. A resultant laminated body is then subjected to heat treatment and then pressure-sintering, whereby a fiber-reinforced composite which has excellent oxidation-resistance, a good mechanical strength characteristic and excellent fracture toughness can be manufactured even if its surface portion sheet is exposed under high temperatures not lower than 1500°C.

Although the present invention has been described and illustrated in detail, it is clearly understood that the same is by way of illustration and example only and is not to be taken by way of limitation, the spirit and scope of the present invention being limited only by the terms of the appended claims.

Claims

1. A fiber-reinforced composite having a gradient function, comprising:

an inner base formed of a fiber-reinforced composite in which a first matrix including heat resisting ceramics is reinforced with carbon fiber; and

two surface portions formed on both surfaces of said inner base and formed of a ceramic-fiber reinforced composite in which a second matrix including heat resisting ceramics is reinforced with ceramic fiber, wherein

the rate of carbon-fiber content of said inner base decreases almost successively from a central portion of said inner base to an interface of said inner base and said surface portions.

2. The fiber-reinforced composite according to claim 1, wherein
said first matrix comprises at least one selected from the group consisting of silicon carbide and silicon nitride, and
said second matrix comprises at least one selected from the group consisting of carbon, silicon carbide, silicon nitride, boron carbide and alumina.

3. The fiber-reinforced composite according to claim 1, wherein
respective thermal expansion coefficients α of said inner base and said surface portions increase almost successively from the central portion of said inner base to said surface portions.

4. The fiber-reinforced composite according to claim 2, wherein
a coated layer including ceramics is formed on at least one of said two surface portions.

5. The fiber-reinforced composite according to claim 4, wherein
said coated layer including ceramics comprises at least one type of ceramics selected from the group consisting of silicon carbide and silicon nitride.

6. A fiber-reinforced composite having a gradient function, comprising:
a base formed of a carbon-fiber reinforced composite in which a first matrix including ceramics is reinforced with carbon fiber; and
a surface portion formed on one surface of said base and formed of a ceramic-fiber reinforced composite in which a second matrix including ceramics is reinforced with ceramic fiber, wherein
the rate of carbon fiber content of said base decreases almost successively from a central portion of said base to an interface of said base and said surface portion.

7. The fiber-reinforced composite according to claim 6, wherein
said first matrix comprises at least one type selected from the group consisting of silicon carbide and silicon nitride, and
said second matrix comprises at least one type selected from the group consisting of carbon, silicon carbide, silicon nitride, boron carbide and alumina.

8. The fiber-reinforced composite according to claim 6, wherein
respective thermal expansion coefficients α of said base and said surface portion increase almost successively from the central portion of said base to said surface portion.

9. The fiber-reinforced composite according to claim 7, wherein
a coated layer including ceramics is formed on said surface portion.

10. The fiber-reinforced composite according to claim 9, wherein
said coated layer including ceramics comprises at least one type of ceramics selected from the group consisting of silicon carbide and silicon nitride.

11. A method of manufacturing a fiber-reinforced composite, comprising the steps of:
forming a plurality of sheets for a base, formed of a carbon-fiber reinforced composite in which a first matrix including ceramics is reinforced with carbon fiber and having different content rates of said carbon fiber;
forming a plurality of sheets for surface portions, formed of a ceramic fiber reinforced composite in which a second matrix including ceramics is reinforced with ceramic fiber;
laminating said plurality of base sheets so that the carbon fiber content rates of said base sheets decrease from a center to the outside, and laminating said surface portion sheets on said base sheets of two outermost layers, so as to form a laminated body; and
subjecting said laminated body to heat treatment and then pressure sintering.

12. The method according to claim 11, wherein
said first matrix comprises at least one type selected from the group consisting of silicon carbide

and silicon nitride, and

said second matrix comprises at least one type selected from the group consisting of carbon, silicon carbide, silicon nitride, boron carbide and alumina.

13. A method of manufacturing a fiber-reinforced composite, comprising the steps of:

forming a plurality of base sheets formed of a carbon fiber reinforced composite in which a first matrix including ceramics is reinforced with carbon fiber and having different content rates of said carbon fiber;

forming a surface portion sheet formed of a ceramic-fiber reinforced composite in which a second matrix including ceramics is reinforced with ceramic fiber;

forming a laminated body by laminating said plurality of base sheets so that the carbon fiber content rates of said base sheets decrease from a center to one outside and also laminating said surface portion sheet on said base sheet of an outermost layer having the carbon fiber content rate decreased; and

subjecting said laminated body to heat treatment and then pressure sintering.

14. The method according to claim 13, wherein

said first matrix comprises at least one type selected from the group consisting of silicon carbide and silicon nitride, and

said second matrix comprises at least one type selected from the group consisting of carbon, silicon carbide, silicon nitride, boron carbide and alumina.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 10 9856

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-4 391 873 (G. W. BRASSELL ET AL.) * claims 1,2 * ---	1,6	B32B5/14 C04B35/80
A	PATENT ABSTRACTS OF JAPAN vol. 010, no. 043 (C-329)20 February 1986 & JP-A-60 190 545 (MITSUBISHI JIDOSHA KOGYO KK) 28 September 1985 * abstract * ---	1,6	
A	DATABASE WPIL Week 8911, Derwent Publications Ltd., London, GB; AN 89-081092 & JP-A-1 033 077 (TOYO KOGYO KK) 2 February 1989 * abstract * ---	1,6	
A	GB-A-2 239 214 (ROLLS-ROYCE P.L.C.) * claims 1,2,10,13,20 * ---	1,11	
A	EP-A-0 355 916 (THE DOW CHEMICAL CO.) * page 3, line 19 - line 43; figures 1,2 * ---	1,2	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	US-A-4 992 318 (K. P. GADKAREE) ---		B32B C04B
A	DE-U-8 801 481 (DIDIER-WERKE A.G.) -----		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	18 NOVEMBER 1992	MCCONNELL C.H.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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